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DOI: 10.1039/C5NJ01597A

Journal Name

ARTICLE

Palladium catalyzed decarboxylative acylation of arylboronic acid with ethyl cyanoacetate as a new acylating agent: synthesis of alkyl aryl ketones

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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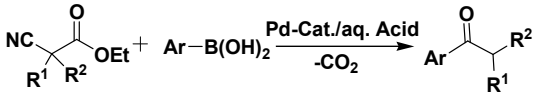
Palladium catalyzed acylation of arylboronic acid containing various functional groups was performed efficiently by ethyl cyanoacetate/substituted ethyl cyanoacetate as acylating agent in aqueous triflic acid medium. The alkyl aryl ketones were obtained in good to excellent yields first by addition of arylboronic acid to nitrile group of ethyl cyanoacetate and their derivatives, followed by *in situ* decarboxylation of the resulting ß-ketoester.

Introduction

Alkyl aryl ketones are common and important intermediates in the agrochemical, pharmaceutical, fragrance, and dye industries.[1] Alkyl aryl ketones are conventionally synthesized by Friedel-Crafts acylation, which involves activation of electrophile with hazardous reagents and further limits to electron rich arenes.[2] Discovery of catalytic transformation, especially the transition metal catalyzed C–C bond formation provides useful alternative to such stoichiometric reactions for the commercial synthesis of important intermediates. Transition metal catalyzed addition of arylboronic acid to nitriles emerged as an improvement over the conventional methods of syntheses of aryl ketones because of wider functional group compatibility and ease of handling. Recently, a significant amount of research has been devoted to addition of arylboronic acids to nitriles catalyzed by rhodium,[3]palladium,[4] and nickel.[5] However, in most cases, the substrate scope is limited to aromatic nitriles and activated nitriles.[3b,3c] Alternative routes for transition metal catalyzed synthesis of unsymmetrical ketones are hydroacylation from reaction of aldehydes and olefins,[6] acylation of aryl halides,[7] and carbonylative cross-coupling reaction.[8] For the synthesis of alkyl aryl ketones from arylboronic acids the use of anhydrides,[9] acid chlorides,[10] and esters[11] as acylating source, were most common unlike that of aliphatic nitriles.[12] This is because electrophilic activation of aliphatic nitrile is not sufficient enough to perform nucleophilic addition reactions and also aliphatic nitriles have tendency to get deprotonated in the presence of palladium catalysts leading to α-arylation products.[13] Thus, the addition reaction to aliphatic nitriles is generally morechallenging than that of aromatic nitriles. On the other hand ethyl cyanoacetate is an inexpensive, nontoxic and easy to handle organic reagent for acylation of arylboronic acid. Functionalization is also possible due to the presence of active methylene hydrogen in ethyl cyanoacetate by most simple technique[14] which opens up broad substrate scope for this method to have wide applications.

In most of the cases of acylation of arylboronic acid[9,10,11] reported earlier, phosphine based ligands were employed. Our initial effort seeking to explore pyrazole tethered donors as effective ligands[15] in metal catalysed reactions led us to identify a non-phosphorus based pyrazole tethered pyridine ligand **L**. This ligand can coordinate with palladium effectively and thereby catalyze an addition reaction of arylboronic acid to aryl aldehydes[16a] and nitriles[16b] in aqueous triflic acid medium. In our previous work[16b] we have observed that aliphatic nitriles in spite of having lower electrophilicity, showed excellent results and when ethyl cyanoacetate was used as nitrile coupling partner with phenylboronic acid, acetophenone was obtained as acylation product of phenylboronic acid via *in situ* decarboxylation of the initially formed ß-keto ester as the medium was acidic. In reference to that we wanted to explore whether ethyl cyanoacetate can be used as acylating agent for arylboronic acid in general. Here in, we describe for the first time decarboxylative acylation of arylboronic acid using ethyl cyanoacetate/substituted ethyl



Scheme 1.Alkyl aryl ketone synthesis by decarboxylative acylation of arylboronic acid by ethyl cyanoacetate/substituted ethyl cyanoacetate.

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cyanoacetate as an acylating agent in presence of non-phosphine based pyrazole-pyridine ligand. This convenient synthesis of alkyl aryl ketones appears to involve both the addition of aryl group of arylboronic acid to nitriles and decarboxylation of the resultant β-ketoester in the same reaction system (Scheme 1).

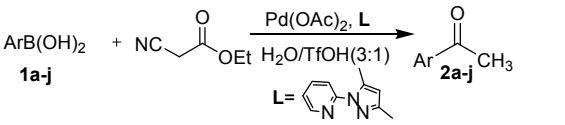
Results and Discussion

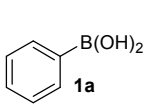
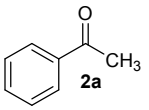
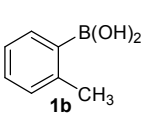
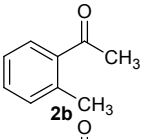
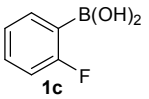
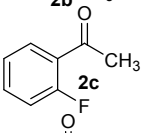
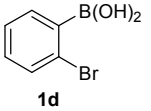
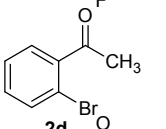
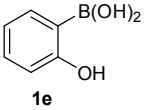
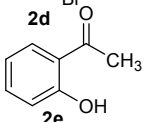
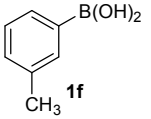
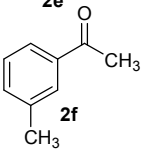
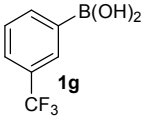
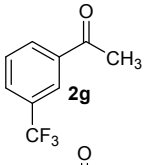
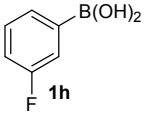
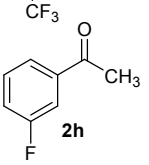
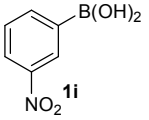
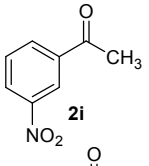
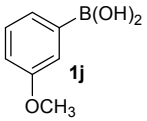
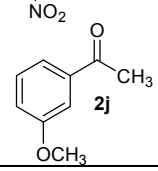
Initially, with a view to generalize the acylation reaction of appropriate commercially available arylboronic acids by ethyl cyanoacetate, the optimized reaction condition mentioned in our recent report[16b] was followed. Subsequently all the reactions were carried out by a general experimental procedure: ethyl cyanoacetate (0.5 mmol), arylboronic acid (0.6 mmol), $Pd(OAc)_2$, (4 mol%) and ligand **L**(4 mol%) in water-trifllic acid mixture (3:1) were heated at 60 °C for 5h and progress of the reaction was monitored by TLC. Standard work up with ethyl acetate followed by purification on silica gel column chromatography afforded the pure products. A large number of electronically and structurally diverse arylboronic acids were explored under this reaction condition and in most of the cases acylated products **2a-u** were obtained in good to excellent yields. Results are summarized in Table 1. Arylboronic acids containing electron donating groups (**1b**, **1e**, **1j**, **1k** and **1t**; Table 1) provided excellent yields except 2-hydroxy phenylboronic acid (**1e**) and 2, 4-dicholoro phenylboronic acid (**1o**) probably because of steric reason. For these two substrates elevation of temperature enhance the yield above 70%. Lack of reactivity in case of electron withdrawing groups substituted phenylboronic acid (**1g**, **1i**; Table 1) can be compensated by increasing the temperature. This is perhaps due to lower nucleophilicity of the aryl group of arylboronic acid which slows down the transmetalation step to cationic Pd(II) complex (*vide infra*, Scheme 2).[17] Sterically hindered arylboronic acids (**1b**, **1e**, **1r**, **1t**, **1u**; Table 1) also afforded products in good to excellent yields. Despite heating in a strongly acidic medium, it is remarkable to note that the desired alkyl aryl ketones were obtained from -OH, -OMe,NO_2, -X (Cl, Br, F) substituted phenylboronic acids in high yields (**1c**, **1d**, **1e**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n, 1o** and **1p** respectively). This offers a clear opportunity for these substrates to undergo further transformation. Acetyl group can also be appended at 3-position of thiophene in very good yield when 3-thiopheneboronic (**1q**) acid was used as starting material (Entry 15, Table 1).

On the other hand, the superior control of the regioselectivity i.e. addition to nitrile, rather than substitution at α-carbon of ethyl cyanoacetate to obtain α-arylcyanoester which is the common product when ethyl cyanoacetate reacts with aryl halide in presence of Pd catalyst and ligand,[13] was observed. For example, arylboronic acid **1c**, **1d**, **1h**, **1l**, **1m**, **1n, 1o** and **1p** containing halide groups were tolerated in our reaction condition giving excellent yields of the desired ketone without any trace of α-arylcyanoester products.

Encouraged by these results, we thought of extending the decarboxylative acylation strategy for substituted ethyl cyanoacetate. For mono substituted small chain ethylcyanoacetate derivative, desired acylation product were obtained but when we switched to the disubstituted, cyclic and long chain derivatives of ethylcyanoacetate, it resulted in desired products along with non-decarboxylative products. However, in case of hexadecyl derivative non-

Table 1. Scope of arylboronic acid substrates in Pd-catalyzed acylation[a]



Entry	Bronic Acid	Product	Time (h)	Yield[b] (%)
1	 **1a**	 **2a**	5	89
2	 **1b**	 **2b**	5	98
3	 **1c**	 **2c**	5	72
4	 **1d**	 **2d**	5	66
5	 **1e**	 **2e**	8	31(80)[c]
6	 **1f**	 **2f**	5	93
7	 **1g**	 **2g**	8	35(71)[c]
8	 **1h**	 **2h**	5	90
9	 **1i**	 **2i**	8	32(68)[c]
10	 **1j**	 **2j**	5	72

[a]Reaction condition: $ArB(OH)_2$ (1.2 mmol), Ethyl cyanoacetate (1 mmol), H_2O/TfOH (1.2 mL/0.4 mL), $Pd(OAc)_2$ (4 mol %), **L** (4 mol %), under air, 60 °C. [b]Isolated yields. [c] At 90 °C.

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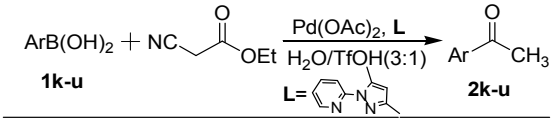
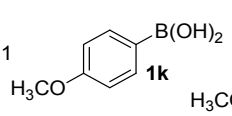
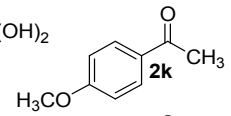
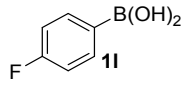
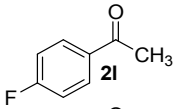
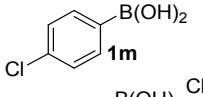
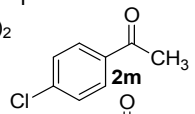
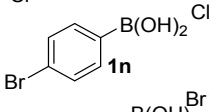
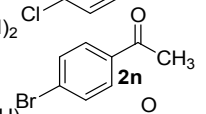
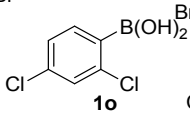
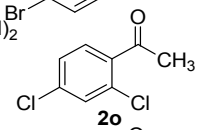
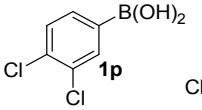
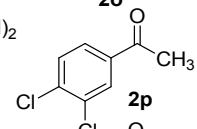
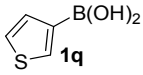
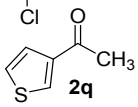
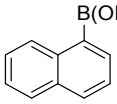
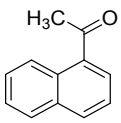
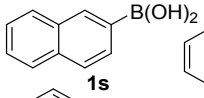
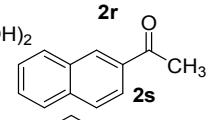
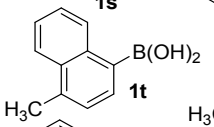
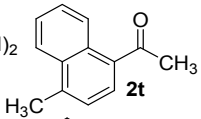
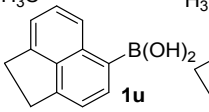
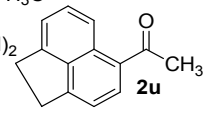
Table 1 Contd.

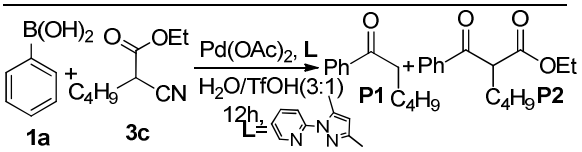


Entry	Bronic Acid	Product	Time (h)	Yield (%)
11			5	82
12			5	81
13			5	73
14			5	86
15			8	34(70)[c]
16			5	91
17			5	80
18			5	98
19			5	91
20			5	85
21			5	98

[a]Reaction condition: $ArB(OH)_2$ (1.2 mmol), ethyl cyanoacetate (1 mmol), H_2O/TfOH (1.2 mL/0.4 mL), $Pd(OAc)_2$ (4 mol %), **L** (4 mol %), under air, 60 °C. [b]Isolated yields. [c]At 90 °C.

decarboxylativeproduct was isolated exclusively. Therefore, it is of particular interest to increase the substrate scope. In a quest to facilitate the decarboxylation for these particular substrates, we freshly screened the reaction of phenylboronic acid and ethyl 2-cyanohexanoate(**3c,** Table 2) with different organic solventsin combination with water and triflic acid. Initially, when ethyl cyanoacetate was reacted with phenylboronic acid following the condition mentioned in Table 1, acylation product was the only isolable product (entry 1, Table 2). But under same condition ethyl 2-cyanohexanoate(**3c**, Table 2) resulted in desired product along with non-decarboxylative product (entry 2, Table 2) and even at high temperature the formation of 1-phenylhexan-1-one i.e. the desired acylation product was not favored also (entry 3,Table 2) making this optimization study specific for hindered ethyl cyanoacetate derivatives. For optimization studies, ethyl 2-cyanohexanoate(**3c**, Table 2) and phenylboronic acid were selected as reaction partners. First, we performed the reaction in dioxane/water/TfOH in 3:3:2 ratio (entry 4, Table 2) but it resulted in homocoupling of phenylboronic acid. Keeping the water-TfOH ratio intact under table 1 condition, when switched to stoichiometric amount of organic solvent, we observed a facile decarboxylaion. In a solvent of high polarity such as in DMSO, DMF, PEG and ethanol, the reaction resulted in moderate yield but in nitromethane the catalytic reaction did not proceed at all.

Table 2. Optimisation studies[a]



Entry	Organic solvent	P1 (%)[b]	P2 (%)[b]
1[c]	-	100	0
2	-	20	80
3[d]	-	30	70
4[e]	-	-	-
5	Dioxane	90	10
6	Dimethylformamide(DMF)	70	30
7	Ethanol(EtOH)	60	40
8	Polyethyleneglycol(PEG-600)	70	30
9	Dimethylsulfoxide(DMSO)	70	30
10	Toluene	60	40
11	**Dimethoxyethane(DME)**	**100**	**0**
12	Nitromethane	0	0
13	Tetrahydrofuran(THF)	85	15
14	Dichloroethane(DCE)	70	30
15[f]	Dimethoxyethane(DME)	0	0
16[g]	Dimethoxyethane(DME)	0	0

[a]Reaction condition : Phenylboronic acid (1.2 mmol), ethyl 2-cyanohexanoate (1 mmol), $Pd(OAC)_2$ (4 mol%), **L** (4 mol%), organic solvent (1 eq.), under air, 60 °C. [b]Product distribution by isolated yield. [c]With ethyl cyanoacetate. [d]At 90 °C [e]Dioxane/H_2O/TfOH (3:3:2), [f]No ligand used, [g]No $Pd(OAc)_2$.

Among other solvents such as toluene, tetrahydrofuran (THF), dimethoxyethane (DME), dioxane and dichloroethane (DCE) respectively, DME is superior. Also, the reaction did not proceed in the absence of the ligand; and the reaction mixture immediatelyturned black indicating precipitation of palladium

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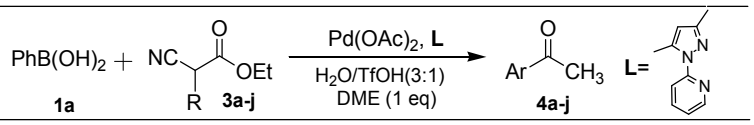
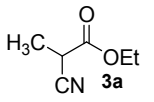
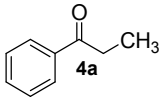
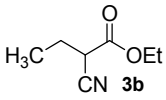
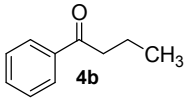
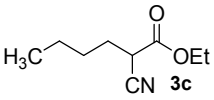
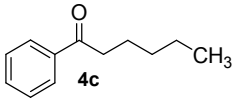
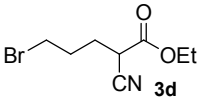
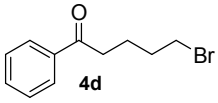
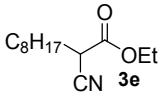
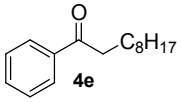
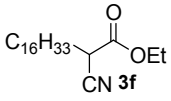
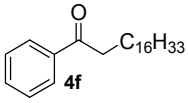
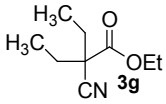
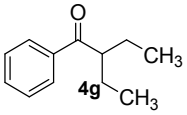
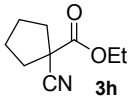
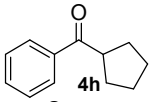
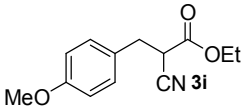
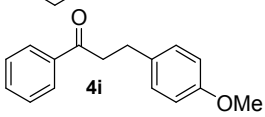
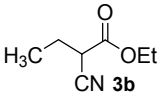
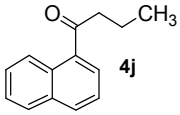
Table3. Scope of ethyl cyanoacetate in Pd-catalyzed acylation of phenylboronicacid[a]



Entry	Ethylcyanoacetate Derivative (R)	Product	Time/h	Yield[b]
1			5	95[c]
2			5	99[c]
3			12	97
4			12	90
5			12	94
6			12	70[d]
7			12	75
8			12	70
9			5	78[c]
10[e]			5	91[c]

[a]Reaction condition: $ArB(OH)_2$ (1.2 mmol), ethyl cyanoacetate derivative (1 mmol), H_2O/TfOH (1.2 mL/0.4 mL), DME (1 eq.), $Pd(OAc)_2$ (4 mol %), L (4 mol %), under air, 60°C. [b]Isolated yield. [c]Reaction was performed under condition of Table 1. [d]At 90°C, [e]1-naphthylboronic acid was used.

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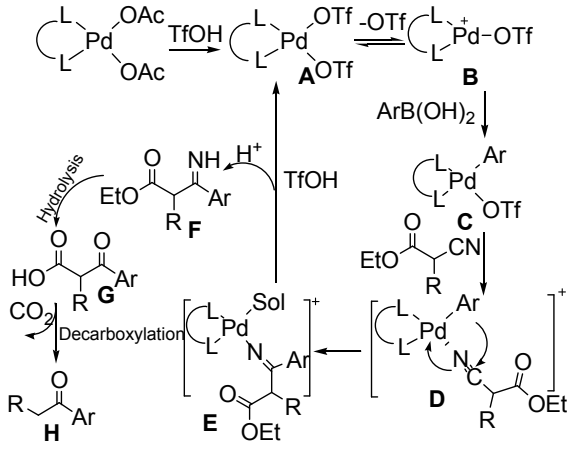
black (entry 15, Table 2).The results of the reaction ofarylboronic acidand substituted ethyl cyanoacetates are presented in Table 3(containing both the conditions of Table 1 and modified optimization condition). Mono substituted small chain alkyl (**3a**, **3b**; Table 3) and benzyl derivative (**3i**, Table 3)of ethyl cyanoacetate afforded almost quantitative yields under optimized reaction condition as described before in Table 1. The bromo alkyl substituted ethyl cyanoacetate (**3d**, Table 3) remained intact under this condition, thus, offering the scope forfurther transformation. The potential of present strategy was further extended to cyclic derivative (**3h**, Table 3) for the synthesis of cyclopentyl(phenyl)methanone (**4h**) ketone. However, the addition reaction of ethyl 2-cyanooctadecanoate and phenyboronic acid required heating to 90 °C, and 1-phenyloctadecan-1-one (**4f**, Table 3), was isolated after 12h in 70% yield.

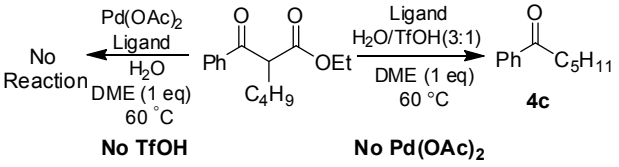
From our earlier observation and on the basis of suggestions made in earlier report,[16b] we can speculate a plausible mechanism of this transformation as shown in Scheme 2. First, electrophilic transmetalation of arylboronic acid occurs by cationic Pd(II) species (**B**)[17] to generate **C**. Then nitrile group coordinates to the vacant coordination site of Pd giving intermediate **D**. Selective intramolecular migration of the aryl group from Pd centre to the activated carbon of the nitrile would result in the new C-C bond formation to afford intermediate **E**. Finally protonolysis of **E** affords **F** and regenerates the [Pd] catalyst. Once **F** is generated, undergoes hydrolysis followed by decarboxylation to give the desired alkyl aryl ketone (Scheme 2).

Scheme 2. Proposed mechanism



In order to confirm the role of TfOH/$Pd(OAc)_2$ during hydrolysis of β-ketoester, we have also performed the reaction starting from separately isolated ethyl 2-benzoylhexanoate following the condition of Table 3(Scheme 3).Result shows that the presence of triflic acid is essential for decarboxylation of the β-ketoester. Only when triflic acid was used, we obtained the desired decarboxylation product (**4c**).

Scheme 3.



Conclusions

In conclusion, the protocol described here disclosed a new variant of acylating agent for acylation of arylboronic acid by an operationally simple, effective yet mild reaction condition thus giving a new avenue for the synthesis of alkyl aryl ketone. Designing of alkyl aryl ketone was enriched by the use of both differently functionalized arylboronic acid and various derivatives of ethylcyanoacetate. Also the method offers several advantages in terms of reaction time, temperature, yield, and convenience. These combined features render the new reaction protocol useful for application in agrochemical and pharmaceutical industries.

Experimental Section

General

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a BrukerAvance III HD (300 MHz) or Avance III HD (400 MHz) or Avance III 500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.16) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). Coupling constants were reported in Hertz (Hz). High resolution mass spectra were obtained on a Micromass/Q-Toff. microTM spectrometer. For thin layer chromatography (TLC), Merck precoated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine. Flash chromatography separations were performed on SRL 230-400 mesh silica gel.

General procedure: To a mixture of arylboronic acid (1.2 mmol),ethyl cyanoacetate (1.0 mmol), $Pd(OAc)_2$ (4 mol%) and **L** (4 mol%), H_2O (1.2 mL) and triflic acid (0.4 mL) were added and stirred at 60 °C under air for desired time (TLC monitoring). Then the reaction mixture was neutralized with saturated $NaHCO_3$ solution and extracted with ethylacetate. The combined ethylacetate solution was washed with brine, dried by Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel using petroleum

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ether/ethylacetate or petroleum ether/DCM as eluent to give the desired product.

Modified procedure for 4c, 4d, 4e, 4f, 4g, 4h of Table 3: To a mixture of arylboronic acid (1.2 mmol),substituted ethyl cyanoacetate (1.0 mmol), $Pd(OAc)_2$ (4 mol%) and **L** (4 mol%), H_2O (1.2 mL), triflic acid (0.4 mL) and dimethoxyethane (1 mmol, 0.1 mL) were added and stirred at 60 °C under air for 12h. Then the reaction mixture was neutralized with saturated $NaHCO_3$ solution and extracted with ethyl acetate. The combined ethyl acetate solution was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel using petroleum ether/Ethyl acetate or petroleum ether/DCM as eluent to give the desired product.

All the compounds describe here were known and further identified by comparing their ^1H and ^{13}C spectroscopic data with reported value and the spectra were included in supporting information.

Acetophenon (2a):[16b]Colorless oil, ^1H NMR(300 MHz, $CDCl_3$): δ 2.61 (s, 3H), 7.44-7.49(m, 2H), 7.54-7.60 (m, 1H), 7.95-7.97 (m, 2H); ^{13}CNMR(75 MHz, $CDCl_3$): δ 26.7, 128.4,128.7, 133.2, 137.2, 198.2;

1-*o*-Tolylethanone (2b):[12a]Colorless oil, ^{1}HNMR(400 MHz, $CDCl_3$): δ 2.53 (s, 3H), 2.58 (s, 3H), 7.23-7.25 (m, 2H), 7.36-7.39 (m, 1H), 7.69 (d, *J*=7.6Hz, 1H);^{13}CNMR(100 MHz, $CDCl_3$): δ 21.7, 29.7, 125.8, 129.4, 131.6, 132.2, 137.9, 138.5, 201.9.

1-(2-Fluorophenyl)ethanone(2c):[28]Colorless oil, ^{1}HNMR(500 MHz, $CDCl_3$): δ2.64 (t, *J* = 5.25 Hz, 3H), 7.11-7.15 (m, 1H), 7.22 (t,*J* = 7.5 Hz, 1H), 7.50-7.54 (m, 1H), 7.86-7.89 (m, 1H);^{13}CNMR(125 MHz, $CDCl_3$): δ31.6 (d, $J_{C,F}$ = 7.5 Hz), 116.8 (d, $J_{C,F}$ = 23.75 Hz), 124.5 (d, $J_{C,F}$ = 2.5 Hz), 130.7, 134.8 (d, $J_{C,F}$ = 8.75 Hz), 162.4 (d, $J_{C,F}$ = 252.5 Hz), 196.1.

1-(2-Bromophenyl)ethanone (2d):[32] Yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.64 (s, 3H), 7.27-7.40 (m, 2H), 7.47 (dd, *J* = 1.6 Hz, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.3, 118.9, 127.4, 128.9, 131.8, 133.8, 141.4, 201.4.

1-(2-Hydroxyphenyl)ethanone(2e):[29]Pale yellow oil, ^{1}HNMR(500 MHz, $CDCl_3$): δ 2.64 (s, 3H), 6.9 (t, *J*=7.7Hz, 1H), 6.98 (d, *J*=8.5Hz, 1H), 7.48 (t, *J*=8Hz, 1H), 7.53 (d, *J*=8Hz, 1H), 12.25 (s, 1H), ^{13}CNMR(100 MHz, $CDCl_3$): δ 26.8, 118.6, 119.1, 119.9, 130.9, 136.2.6, 162.6, 204.7.

1-*m*-Tolylethanone (2f):[12a]Colorless oil, ^{1}HNMR(500 MHz, $CDCl_3$): δ 2.41 (s, 3H), 2.59 (s, 3H), 7.32-7.38 (m, 2H), 7.74-7.77 (m, 2H), ^{13}CNMR(125 MHz, $CDCl_3$): δ 21.5, 26.8, 125.7, 128.6, 128.9, 134.0, 137.4, 138.5, 198.5.

1-(3-(Trifluoromethyl)phenyl)ethanone(2g):[20]Colorless oil, ^{1}HNMR(500 MHz, $CDCl_3$): δ 2.65 (s, 3H), 7.61 (t, *J* = 7.75 Hz, 2H), 7.82 (d, *J*= 8 Hz, 1H), 8.13 (d, *J* = 8 Hz, 1H), 8.20 (s, 1H);^{13}CNMR(100 MHz, $CDCl_3$): δ26.7, 122.5, 125.3 (t, $J_{C,F}$ = 4 Hz), 127.9, 129.4, 129.6 (t, $J_{C,F}$ = 3.5 Hz), 131.4 (q, $J_{C,F}$ = 35 Hz), 137.8, 196.7.

1-(3-Fluorophenyl)ethanone (2h):[28]Colorless oil, ^{1}HNMR(400 MHz, $CDCl_3$): δ 2.59 (s, 3H), 7.24-7.41 (m, 1H), 7.41-7.46 (m, 1H), 7.60-7.64(m, 1H), 7.72 (d, *J* = 7.6Hz, 1H), ^{13}CNMR(100 MHz, $CDCl_3$): δ 26.8, 115.1(d, $J_{C,F}$ = 22 Hz), 120.2(d, $J_{C,F}$ = 20 Hz), 124.2(d, $J_{C,F}$ = 2 Hz), 130.4(d, $J_{C,F}$ = 8 Hz), 139.4($J_{C,F}$ = 5 Hz), 164.2(d, $J_{C,F}$ = 246 Hz), 196.8.

1-(3-Nitrophenyl)ethanone (2i):[26]White solid, ^{1}HNMR(400 MHz, $CDCl_3$): δ 2.69 (s, 3H), 7.69 (t, *J* = 7.8Hz, 1H), 8.29 (d, *J* = 8.8Hz, 1H), 8.43 (dd, *J* = 1Hz, *J* = 7.4Hz, 1H), 8.78 (t, *J* = 2Hz, 1H);^{13}CNMR(100 MHz, $CDCl_3$): δ 26.8, 123.4, 127.6, 130.0, 133.9, 138.5, 195.7.

1-(3-Methoxyphenyl)ethanone (2j):[25]Colorless oil, ^{1}HNMR(400 MHz, $CDCl_3$): δ 2.59 (s, 3H), 3.86 (s, 3H), 7.10-7.12 (m, 1H), 7.37 (t, *J* = 8Hz, 1H), 7.48 (t, *J* = 1.6Hz, 1H), 7.53 (d, *J* = 8Hz, 1H);^{13}CNMR(100 MHz, $CDCl_3$): δ 26.8, 55.6, 112.5, 119.7, 121.2, 129.7, 138.7, 160.0, 198.0.

1-(4-Methoxyphenyl)ethanone (2k):[12a]Colorless oil, ^{1}HNMR(400 MHz, $CDCl_3$): δ 2.54 (s, 3H), 3.86 (s, 3H), 6.91-6.93 (m, 2H), 7.92-7.94 (m, 2H), ^{13}CNMR(100 MHz, $CDCl_3$): δ 26.4, 55.6, 113.8, 130.5, 130.7, 163.6, 196.9.

1-(4-Fluorophenyl)ethanone (2l):[25]Colorless oil, ^{1}HNMR(500 MHz, $CDCl_3$): δ 2.58 (s, 3H), 7.10-7.14 (m, 2H), 7.96-7.99 (m, 2H), ^{13}CNMR(100 MHz, $CDCl_3$): δ 26.6, 115.8 (d, $J_{C,F}$ = 22 Hz), 131.1 (d, $J_{C,F}$ = 9 Hz), 133.8 (d, $J_{C,F}$ = 3 Hz), 165.9 (d, $J_{C,F}$ = 253 Hz), 196.6.

1-(4-Chlorophenyl)ethanone (2m):[12a]Colorless oil, ^{1}HNMR(500 MHz, $CDCl_3$): δ 2.58 (s, 3H), 7.42-7.44 (m, 2H), 7.88-7.89 (m, 2H);^{13}CNMR(100 MHz, $CDCl_3$): δ 26.6, 129.0, 129.9, 135.6, 139.7, 196.9.

1-(4-Bromophenyl)ethanone (2n):[32] White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.57 (s, 3H), 7.59 (d, *J* =8.8 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.6, 128.4, 129.91, 129.94, 132.0, 136.0, 197.1.

1-(2,4-Dichlorophenyl)ethanone (2o):[20]Colorless sticky oil, ^{1}HNMR(500 MHz, $CDCl_3$): δ 2.64 (s, 3H), 7.32 (d, *J* = 8.5Hz, 1H), 7.45 (d, *J* = 1.5Hz, 1H), 7.54 (d, *J* = 8Hz, 1H);^{13}CNMR(100 MHz, $CDCl_3$): δ 30.8, 127.5, 130.7, 130.8, 132.7, 137.4, 137.9, 199.0.

1-(3,4-Dichlorophenyl)ethanone (2p):[21]White solid, ^{1}HNMR(400 MHz, $CDCl_3$): δ 2.58 (s, 3H), 7.54 (d, *J* = 8.4Hz, 1H), 7.77 (dd, *J* = 2Hz, *J* = 8.4Hz 1H), 8.02 (d, *J* = 2Hz, 1H), ^{13}CNMR(100 MHz, $CDCl_3$): δ 26.7, 127.5, 130.5, 130.9, 133.5, 136.8, 137.9, 195.8.

1-(Thiophen-3-yl)ethanone (2q):[27]Pale yellow oil, ^{1}HNMR(500 MHz, $CDCl_3$): δ 2.54 (s, 3H), 7.30-7.32 (m, 1H) 7.54 (d, *J* = 5Hz, 1H), 8.04 (d, *J* = 2Hz, 1H);^{13}CNMR(100 MHz, $CDCl_3$): δ 27.7, 126.5, 127.1, 132.4, 142.8, 192.4.

1-(Naphthalen-1-yl)ethanone (2r):[12a]Pale yellow oil, ^{1}HNMR(500 MHz, $CDCl_3$): δ 2.75 (s, 3H), 7.48-7.55 (m, 2H), 7.61 (t, *J* = 2.8Hz, 1H), 7.87 (d, *J* = 8Hz, 1H), 7.94 (d, *J* = 7Hz, 1H), 7.99 (d, *J* = 8.5Hz, 1H), 8.75 (d, *J* = 8.5Hz, 1H);^{13}CNMR(125 MHz, $CDCl_3$): δ 30.1, 124.5, 126.2, 126.6, 128.2, 128.5, 128.8, 130.3, 133.1, 134.1, 135.7, 202.0.

1-(Naphthalen-2-yl)ethanone (2s):[12a]Yellowish solid, ^{1}HNMR(400 MHz, $CDCl_3$): δ 2.73 (s, 3H), 7.54-7.62 (m, 2H), 7.87-7.90 (m, 2H), 7.97 (d, *J* = 8Hz, 1H), 7.94 (d, *J* = 7Hz, 1H), 7.99 (d, *J* = 8.5Hz, 1H), 8.75 (d, *J* = 8.5Hz, 1H) 8.46 (s, 1H);^{13}CNMR(125 MHz, $CDCl_3$): δ 26.8, 124.0, 126.9, 127.9, 128.5, 128.6, 129.7, 130.3, 132.7, 134.7, 135.7, 198.2.

1-(4-Methylnaphthalen-1-yl)ethanone (2t):[25]Pale yellow sticky oil,^{1}HNMR(400 MHz, $CDCl_3$): δ 2.73 (s, 3H), 2.74 (s, 3H), 7.34 (d, *J* = 7.6Hz, 1H), 7.57-7.63 (m, 2H), 7.85 (d, *J* = 7.2Hz, 1H), 8.03-

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DOI: 10.1039/C5NJ01597A

8.05 (m, 1H), 8.85 (d, *J* = 8Hz, 1H);[13]CNMR(125 MHz, $CDCl_3$): *δ* 20.2, 29.9, 124.4, 126.2, 126.6, 128.2, 128.5, 128.8, 130.3, 133.1, 134.1, 135.7, 202.0.

1-(1,2-Dihydroacenaphthylen-5-yl)ethanone (2u):[19]Pale yellow solid,[1]HNMR(500 MHz, $CDCl_3$): *δ* 2.73 (s, 3H), 3.38-3.43(q, 4H), 7.29 (d, *J*=8Hz, 1H), 7.36 (d, *J*=6.5Hz, 1H), 7.60 (t, *J*=7.75Hz, 1H), 8.06 (d, *J*=7.5Hz, 1H), 8.73 (d, *J*=8.5Hz, 1H), [13]CNMR(100 MHz, $CDCl_3$): *δ* 29.1, 30.5, 30.6, 118.2, 120.5, 122.6, 127.6, 129.4, 130.2, 130.5, 133.0, 139.8, 146.1, 153.2, 200.3. HRMScalcd.for $C_{14}H_{13}O$ $[M+H]^+$: 197.0966, found: 197.0962.

Propiophenone (4a):[4c]Colorless oil, [1]HNMR(500 MHz, $CDCl_3$): *δ* 1.23(t, *J*=7Hz, 3H), 3.00 (q,*J* = 7.25 Hz, 2H), 7.45 (t, *J* = 8 Hz, 2H), 7.55 (t,*J* = 7.25 Hz, 1H), 7.96 (d, *J*=8Hz, 2H); [13]CNMR(100 MHz, $CDCl_3$): *δ* 8.4, 31.9, 128.1, 128.7, 133.0, 137.1, 200.9.

1-Phenylbutan-1-one (4b):[16b]Colorless oil, [1]HNMR(500 MHz, $CDCl_3$): *δ* 1.01(t, *J*=7Hz, 3H), 1.75-80 (m, 2H), 2.95 (t, *J*=7Hz, 2H), 7.44-7.47(m, 2H), 7.53-7.56 (m, 1H), 7.96 (d, *J*=8Hz, 2H); [13]CNMR(100 MHz, $CDCl_3$): *δ* 14.0, 17.9, 40.7, 128.2, 128.7, 133.0, 137.3, 200.5.

1-Phenylhexan-1-one (4c):[18]Pale yellow oil,[1]HNMR(400 MHz, $CDCl_3$): *δ* 0.91(t, *J*=8.7Hz, 3H), 1.34-1.39 (m, 4H), 1.70-1.78 (m, 2H), 2.95 (t, *J*=9.2Hz, 2H), 7.45(t, *J*=9.5Hz, 2H), 7.54 (t, *J*=9Hz, 1H), 7.96 (d, *J*=9Hz, 2H); [13]CNMR(100 MHz, $CDCl_3$): *δ* 14.1, 22.6, 24.2, 31.7, 38.7, 128.2, 128.7, 132.9, 137.3, 200.7; HRMS calcd. for $C_{12}H_{17}O$ $[M+H]^+$: 177.1279, found: 177.1276.

5-Bromo-1-phenylpentan-1-one (4d):[23] White solid,[1]HNMR(500 MHz, $CDCl_3$): *δ* 1.88-2.00 (m, 4H), 3.02 (t, *J*=7Hz, 2H), 3.46 (t, *J*=6.3Hz, 2H), 7.47(t, *J*=7.5Hz, 2H), 7.57 (t, *J*=7.5Hz, 1H), 7.96 (dd, *J*= 1 Hz, *J*= 8.25 Hz, 2H); [13]CNMR(125 MHz, $CDCl_3$): *δ* 22.9, 32.4, 33.4, 37.6, 128.2, 128.8, 133.2, 137.0, 199.7.HRMScalcd.for $C_{11}H_{14}BrO$ $[M+H]^+$: 241.0228, 243.0208, found: 241.0224, 243.0218.

1-Phenyldecan-1-one(4e):[22] Colorless oil, [1]HNMR(500 MHz, $CDCl_3$): *δ* 0.88 (t, *J*= 6.75 Hz, 3H), 1.27-1.39 (m, 12H), 1.70-1.76 (m, 2H), 2.95 (t, *J*=7.25Hz, 2H), 7.44 (t, *J*=7.75Hz, 2H), 7.54 (t, *J*=7.5Hz, 1H), 7.95 (d, *J*=8Hz, 2H); [13]CNMR(125 MHz, $CDCl_3$): *δ* 14.2, 22.8, 24.5, 29.4, 29.5, 29.6, 32.0, 38.7, 128.2, 128.6, 132.9, 137.3, 200.6. HRMS calcd.for $C_{16}H_{25}O$ $[M+H]^+$: 233.1905, found: 233.1902.

1-Phenyloctadecan-1-one (4f):[30] White solid, [1]HNMR(500 MHz, $CDCl_3$): *δ* 0.88 (t, *J*= 7 Hz 3H), 1.21-1.39 (m, 28H), 1.72-1.76 (m, 2H), 2.96 (t, *J*= 7.25 Hz, 1H), 7.46 (t, *J*= 7.5 Hz, 2H), 7.55 (t, *J*=7.25 Hz, 1H), 7.96 (d, *J*= 8.5 Hz, 2H); [13]CNMR(100 MHz, $CDCl_3$): *δ* 14.2, 22.8, 24.6, 29.5, 29.55, 29.6, 29.7, 29.77, 29.8, 29.84, 32.1, 38.8, 128.2 128.7, 133.0, 137.3, 200.7.

2-Ethyl-1-phenylbutan-1-one (4g):[24]Colorless oil, [1]HNMR(500 MHz, $CDCl_3$): *δ* 0.88 (t,*J*=7.5Hz, 4H), 1.54-1.59 (m, 2H), 1.77-1.82 (m, 2H), 3.29-3.32 (m, 1H), 7.47 (t, *J*=7.5Hz, 2H), 7.56 (t, *J*=7.25Hz, 1H), 7.96 (d, *J*=8.5Hz, 2H); [13]CNMR(125 MHz, $CDCl_3$): *δ* 12.0, 25.0, 49.4, 128.3, 128.7, 132.9, 138.1, 204.7.

Cyclopentyl(phenyl)methanone (4h):[24]Colorless sticky oil, [1]HNMR(500 MHz, $CDCl_3$): *δ* 1.36-1.54 (m, 4H), 1.72-1.90 (m, 4H), 3.26 (tt, *J*= 3Hz, *J*= 11.25 Hz, 1H), 7.44-7.47 (m, 2H), 7.52-7.56 (m, 1H), 7.93-7.95 (m, 2H); [13]CNMR(125 MHz, $CDCl_3$): *δ*26.0, 26.1, 29.6, 45.8, 128.4, 128.7, 132.8, 136.6, 204.0.

3-(4-Methoxyphenyl)-1-phenylpropan-1-one(4i):[18] white solid,[1]HNMR(400 MHz, $CDCl_3$): *δ* 3.02 (t, *J*=7.6Hz, 2H), 3.27 (t, *J*=7.6Hz, 2H), 3.80 (s, 3H), 6.85 (d, *J*=8.4Hz, 2H), 7.17 (d, *J*=8.4Hz, 2H), 7.45 (t, *J*=7.8Hz, 2H), 7.56 (t, *J*=7.2Hz, 1H), 7.96 (d, *J*=8.4Hz, 2H); [13]CNMR(100 MHz, $CDCl_3$): *δ* 29.5, 40.9, 55.4, 114.1, 128.2, 128.7, 129.5, 133.2, 133.5, 137.1, 158.2, 199.5.

1-(Naphthalen-1-yl)butan-1-one (4j):[31]Pale yellow sticky oil, [1]HNMR(500 MHz, $CDCl_3$): *δ* 1.04 (t, *J*=7.25Hz, 3H), 1.81-1.85 (m, 2H), 3.04 (t, *J*=7.5Hz, 2H), 7.26-7.53 (m, 2H), 7.57-7.60 (m, 1H), 7.84 (d, *J*=7Hz, 1H), 7.88 (d, *J*=8Hz, 1H), 7.99 (d, *J*= 8.5 Hz, 1H), 8.55 (d, *J*=8.5Hz, 1H);[13]CNMR(100 MHz, $CDCl_3$): *δ* 14.0, 18.3, 44.3, 124.5, 125.9, 126.5, 127.2, 127.9, 128.5, 130.3, 132.4, 134.1, 136.7, 205.1.

Acknowledgements

Authors acknowledge Prof. AmitabhaSarkar (IACS, Kolkata) for his generous suggestions and support. M.Y. and T.D. are thankful to CSIR, India and IACS, Kolkata, respectively for research fellowships. S.A. acknowledges DST (project no. SR/S1/OC-101/2012) for financial support.

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DOI: 10.1039/C5NJ01597A

Graphical Abstract Text

The versatile, one-pot synthesis of a series of alkyl aryl ketones is described using ethyl cyanoacetate as a new acylating agent.